3F19

TOXICITY OF SEDIMENTS AND PORE-WATERS AND THEIR POTENTIAL IMPACT ON NEOSHO MADTOM, *NOTURUS PLACIDUS*, IN THE SPRING RIVER SYSTEM AFFECTED BY HISTORIC ZINC-LEAD MINING AND RELATED ACTIVITIES IN JASPER AND NEWTON COUNTIES, MISSOURI; AND CHEROKEE COUNTY, KANSAS

FINAL REPORT TO THE U.S. FISH AND WILDLIFE SERVICE

COLUMBIA, MISSOURI

Prepared by:

ANN L. ALLERT, MARK L. WILDHABER, CHRISTOPHER J. SCHMITT,

DUANE CHAPMAN, AND ED CALLAHAN

U.S. GEOLOGICAL SURVEY, BIOLOGICAL RESOURCES DIVISION

ENVIRONMENTAL AND CONTAMINANTS RESEARCH CENTER

4200 NEW HAVEN RD., COLUMBIA, MISSOURI 65201

JULY, 1997

Executive Summary

The Tri-State Mining District, comprising portions of Jasper and Newton Counties, Missouri; Cherokee County, Kansas; and Ottawa County, Oklahoma, was mined intensively for zinc and lead for more than 100 yr. Wastes from historic mining, smelting, and related activities have contaminated surface and ground waters. The Tri-State District is drained by the Spring-Neosho River system, which supports populations of the Neosho madtom (*Noturus placidus*), a federally listed threatened fish species (Williams et al. 1989; Wenke and Eberle 1991). This study was designed and implemented to determine the toxicity of pore-water collected in potentially suitable *N. placidus* habitat in the Spring River system affected by mining. Pore-water was collected from sites in the Spring River and its tributaries to assess toxicity to standard test organisms. Pore-water toxicity testing provides a means for assessing sediment quality.

A field study was conducted in September, 1995 to determine the toxicity of pore-water and sediments in the Spring River and two tributaries. Sites were also sampled in an effort to better characterize the Neosho madtom habitat preferences, and benthic macroinvertebrate samples were collected and analyzed to determine associations between these organisms and *N. placidus* abundance and distribution. Samples of surface and interstitial (pore) waters were collected and analyzed for a suite of water quality parameters and for mining-derived metals, and to be used in toxicity tests. The physical characteristics of the sites were also quantified.

Biological sampling revealed that, consistent with previous studies, Neosho madtoms were generally most abundant on gravel bars containing proportionally greater amounts of fine material and lesser amounts of coarse gravel and stones. In the Spring River, this study confirmed the extension of the known range of the species from the confluence of Willow Creek, in Baxter

Springs, Cherokee County, Kansas, upstream to Waco, Jasper County, Missouri (Wilkinson et al. 1996). It may also occur as far upstream in Jasper County as the confluence of the Spring River mainstem and its North Fork but our sampling did not find any *N. placidus* at those locations. Length-frequency distributions indicated the presence of young-of-the-year at several Spring River sites, but the whereabouts of spawning sites and other aspects of the reproductive biology of the Spring River population remain unknown. *N. placidus* has not been found in any Spring River tributary sampled to date, nor has it been found in the Spring River downstream of Baxter Springs. A combination of physical, biological, and chemical factors may presently limit the distribution and abundance of the Neosho madtom in the Spring River. Among the latter, concentrations of zinc and other mining-derived metals in the Spring River below Center Creek, and in both Shoal and Center Creeks may be sufficiently high to affect *N. placidus*.

Background and Purpose

The Tri-State Mining District comprises portions of Jasper and Newton Counties, in southwestern Missouri; Cherokee County, in southeastern Kansas; and Ottawa County, in northeastern Oklahoma. The contamination of surface waters, shallow ground waters, and aquatic biota by zinc and other metals from mining and ore beneficiation in this mineralized area are well documented (Proctor et al. 1974; Pita and Hyne 1975; Czarneski 1985; Smith 1988; Neuberger et al. 1990; Davis and Schumacher 1992; Schmitt et al. 1993a,b). Cherokee and Jasper counties are Superfund sites on the U.S. Environmental Protection Agency (EPA) National Priorities List (NPL). Human health effects were attributed to mining-derived metals in the drinking water supply of Galena, Kansas, which is in Cherokee County (Neuberger et al. 1990);

mining sites in Galena have been remediated. Studies completed and underway in Cherokee County (e.g., Spruill 1987; Ferrington et al. 1988; Dames and Moore 1993a) have also shown effects on aquatic ecosystems from elevated metals and low pH emanating from sites contaminated with wastes from mining and related activities. The Tri-State Mining District is drained in its entirety by the Neosho-Spring River system, which currently supports the only remaining population of the Neosho madtom, *Noturus placidus* (Pisces, Ictaluridae), a federally listed threatened species (Williams et al. 1989; Wenke and Eberle 1991). Schmitt et al. (1997) characterized the availability, quality, and location of physically suitable habitat for Neosho madtoms in the portions of the Spring River and its tributaries potentially affected by mining. Sites were selected to characterize the extent and quality of *N. placidus* habitat in the mining portions of the Spring River system.

Objective 1: Determine the toxicity of pore-water collected in potentially suitable *N. placidus* habitat in the Spring River system affected by mining. Pore-water was collected from sites in the Spring River and its tributaries to assess toxicity to standard test organisms. Pore-water toxicity testing provides a means for assessing sediment quality.

Objective 2: Determine the relative impact of the tributaries on the distribution of Neosho madtom in the Spring River system. Sites on the Spring River were selected above and below several tributaries to examine the impact of the tributaries to habitat, water quality, metal concentration in sediments and water, and toxicity to a standard test organism.

Methods

Site Selection: Sampling sites meeting the general requirements of *N. placidus* within its general known range were identified for consideration. Sites were selected on the basis of gravel presence, accessibility to sampling teams, and historic evidence of *N. placidus* occurrence; i.e., gravel bars where the species was historically present were sampled, as were some previously found to be devoid of *N. placidus*. Sites included those historically sampled by the U.S. Fish and Wildlife Service (FWS) and known to support the species; sites in the Spring River system affected to varying degrees by mining; and sites in the lower reaches of Spring River tributaries, where *N. placidus* has not been found (Figure 1, Table 1). Additional sites were selected and established in a manner consistent with the site selection and sampling protocol used by the FWS, as follows: Based on the known distribution and habitat preferences of *N. placidus*, we defined a site as a gravel bar-riffle complex. At each site, three transects were delineated to bracket all potential *N. placidus* habitat, which we defined as the wadeable portions of the flowing stream (i.e., ≤ 1.25 m deep) associated with the bar. For bars extending completely across the stream, three stations equally spaced across the stream were defined on each transect and marked with floats. Stations were separated by at least 2 m, fewer stations were established for narrow transects. For bars occupying only one bank, the stations were spaced equally by at least 2 m across the portion of the stream that could be waded from the bar (≤ 1.25 m deep).

Field procedures: At each station, physical habitat quality measurements, based on the guidelines and procedures provided by Platts et al. (1983) and Hamilton and Bergersen (1984); water quality; and biological sampling were conducted. To avoid sampling previously disturbed substrate, all sampling proceeded upstream and away from the bank, and the procedures were implemented in the following order: Fishes were collected by kick-seining a 4.5-m × 4.5-m area with a 3-mm (square) mesh seine; benthic invertebrates were collected with a 0.1- m^2 modified Hess sampler equipped with a 0.3-mm mesh collection bag; substrate samples (for particle size analysis) was collected with a 1.1-L [13-cm (depth) × 10-cm (dia.)] cylindrical grab sampler. The depth and current velocity at the substrate and at 60% depth were then measured with a hand-held current meter mounted on a wading rod (Swoffer® Instruments Model 2100) at each station. The dimensions of the site were then determined by direct measurement and the site was diagramed The geospatial coordinates of the upstream and downstream limits of the site were determined with a global positioning system (GPS) receiver (Rockwell® PLGR+®) for future mapping

All equipment used during sediment and water collection was acid-cleaned following standard procedures (Schmitt 1994a,b). Composite samples of surficial streambed sediments representing each site were collected from the upper 4 cm of depositional zones using a PVC scoop; eroding banks and other active areas were avoided. Overlying water was gently decanted from the scoop The sediments from each site were composited into a polyethylene bucket and gently mixed with a Teflon® spoon. Aliquants of composited sediment were transferred with the spoon to three pore-water extractors (Carr and Chapman 1995), and pore-water was extracted under positive pressure (N_2 @ ≤ 30 PSI =1551 torr) into 250-mL polyethylene bottles Pore-water samples were filtered in the field @ 600 mL/ min using an Geofilter® positive-pressure apparatus (Geotech, Denver, CO) through a 142-mm (dia.), 0.45-µm polycarbonate membrane filter; collected in polyethylene bottles; preserved by acidification to 1% (v/v) with nitric acid (Baker® Ultrex); and placed on ice for transport back to the laboratory. An equivalent volume of ultrapure water was carried through the extraction and filtration procedure as a field blank. Using the spoon, a pre-cleaned 4-oz jar (I-Chem) was filled to capacity with a portion of the remaining sediment, capped tightly, and also placed on ice for transport back to the laboratory.

A grab-sample of surface water was collected at the middle station of the most downstream transect defining each site for nutrient and metal analysis. Conductivity, temperature, pH, and dissolved oxygen concentration of surface waters were also measured *in-situ* with water quality instruments (YSI®, Orion®).

In accordance with Endangered Species Subpermit requirements, all ictalurids were released alive, and no voucher specimens were retained. Selected ictalurid specimens were photographed for taxonomic verification, however. For taxa other than Ictaluridae, voucher specimens were preserved in ethanol and returned to the laboratory for confirmation of identification. Fishes were identified according to the criteria presented by Cross (1967), Pflieger (1975), Mayden (1988), Robinson and Buchanan (1988), and Cross and Collins (1995), with specimens assigned to subspecies according to the coding system developed and used by the Missouri Department of Conservation (MDC, Columbia, MO). Identifications of preserved specimens were confirmed by W.L. Pflieger of MDC, and occurrences were further checked against distributional maps provided by Pflieger (1975), Lee et al. (1980), Robinson and Buchanan (1988), and Cross and Collins (1995). Benthic invertebrate samples were preserved in ethanol for laboratory sorting and identification. Substrate samples were wet-sieved (38.1-, 19.0-, 9.5-, and 2-mm sieves) and the fractions were weighed in the field; all material passing the final sieve (2 mm) was retained for further particle size analysis in the laboratory.

Laboratory Procedures: Water quality analyses (i.e., nutrients, major ions, turbidity, etc.) for pore- and surface-water samples were performed by MSC personnel within 12 h of collection. Analyses followed procedures outlined in Standard Methods (APHA 1992). Lead and cadmium in pore-water and surface water were analyzed by atomic absorption spectroscopy by MSC and EPA-Region VII, respectively. All other elements in pore-water and surface water were analyzed using inductively coupled argon plasma (ICAP) emission spectroscopy by MSC and EPA-Region VII, respectively. Sediment analyses were conducted by EPA-Region VII (ICAP) and MSC [acid volatile sulfides (AVS) and simultaneously extracted metals (SEM)]. All containers and sampling equipment used to collect and store metals samples were acid-cleaned, as outlined in the Study Plan, Quality Assurance Project Plan, and Standard Operating Procedures for this investigation (Schmitt 1994a,b).

Relative risk of sediments from different sites were evaluated using the Toxic Units model developed by Wildhaber and Schmitt (1996). A toxic unit is defined as the ratio of the estimated concentration of a contaminant in the pore-water of a test sediment to the estimated chronic toxicity of that contaminant in the water as represented by the formula

Toxic Unit =

C_{wqs}

$\hat{C}_{wp}$ = Estimated pore-water concentration

C_{wqs} = Water quality standard

The estimated pore-water concentrations are considered estimates of the bioavailable portions of the total concentrations of each contaminant as measured in the sediment. Toxic Units for the contaminants (here, just metals) are summed to produce a total toxicity estimate for that sediment.

Pore-water concentrations of metals were estimated from the bulk sediment concentrations by correcting for AVS by using the concentrations of metals simultaneously extracted with AVS adjusted for AVS (DiToro et al. 1990). Estimated pore-water concentrations are calculated by multiplying the estimated bioavailable concentration by the dry weight-to-moisture content ratio of the sediment. Only those metals extractable with a weak acid (1-N HCl) and adjusted by potential sulfide salts that could be formed by the extracted metals are considered bioavailable. For analytes in water quality standards that are dictated by hardness (i.e., cadmium, lead, zinc) the hardness values used in the calculations for individual sediments were those measured in the surface water from each site.

The AVS model is based on the assumption that under the reducing conditions present within sediments, sulfides control pore-water concentrations and hence bioavailability of divalent metals. Sulfide salts of the metals are relatively insoluble; the formation of these salts thereby renders the divalent metals relatively unavailable. AVS was allotted to metals in the following order: copper, cadmium, lead, zinc, nickel and iron. Water quality standards were based on EPA standards (1984a, b, c; 1987) and are listed in Appendix A, Table A1

In the laboratory, the total mass of the dried, 2-mm fraction of each substrate sample was determined. The percentages of sand-, silt-, and clay-sized particles were determined by the Bouyoucos density gradient method. Particle size was also determined for each sediment sample collected for metal analysis. Benthic invertebrate samples were sub-sampled and analyzed by an expedited procedure: From each site, a maximum of three samples (one from each of three transects) was chosen at random. The selected samples were randomly sub-sampled and sorted by a procedure modified from Plafkin et al. (1989). Organisms sorted from these sub-samples were then identified to the lowest taxon possible without mounting individual specimens for compound microscopy. References used to identify invertebrates included Brown (1972), Lewis (1974), Schuster and Etnier (1978), Bednarik and McCafferty (1979), Morihara and McCafferty (1979), Wiederholm (1983), Merritt and Cummins (1984), Schefter and Wiggins (1986), Pennak (1989), Poulton and Stewart (1991), and Thorp and Covich (1991).

Toxicity tests were conducted at MSC using pore-waters collected from each site. Standard test procedures using *Ceriodaphnia dubia* as the test organism include a dilution series with five concentrations for each site water. Ten replicates are run for each dilution, with each replicate renewed daily with 15 mL of water. Ten replicates are also run for controls using dilution and culture waters. Organisms are fed 1.0 μL of a mixture of Yeast-Trout chow-Cerophyll leaves (YTC), and 1.0 μL of algae. Standard procedures were modified for this study due to the limited amount of pore-water collected. Four dilutions (100, 50, 25, 12.5%) were tested for each site water, except at Sites 1 and 2; only three dilutions (50, 25, 12.5%) could be tested. Daily renewals of 10 mL were made. *C. dubia* were fed 0.66 μL of YTC and 0.66 μL of algae. MSC well-water and Tavern Creek pore-water were used as controls. MSC well-water was used for a dilution water.

Results

Physical - Chemical Habitat Analyses The site means of the chemical and physical habitat variables measured at the 12 sites are given in Tables 2-12. Values for individual stations are presented in Appendix A, Tables A2-A3. Average depths were generally greater at sites in the Spring River and Shoal Creek than in Center Creek (Table 2). Current velocities were highest at Shoal Creek sites. Greater than 80% of the substrate particles in riffle sediments were classified as > 9 mm dia. at all but two sites (Sites 4 and 12). Very little clay was found in the riffle sediments at any station at any of the sites. Particle size analysis of sediment collected for chemical analysis in the depositional areas was predominately sand (> 70%) except at Site 12 (Appendix A, Table A4). Sediment from Site 12 was predominately clay (> 54%). The range of of average temperatures was greatest among Spring River samples (13.1 - 25.0°C). Temperatures in Shoal and Center Creek were similar (15.0 -17.5°C and 14.0 -15.0°C, respectively). Surface water were alkaline at all sites (135 - 190 mg/L, pH 7.60 - 8.20) and moderately hard to hard (144 - 184 mg/L) (Table 3). Turbidity were greatest at the Spring River sites, but variable (5.7 - 24.0 NTU). Turbidities in the tributaries were all low (< 10 NTU).

Metal Analyses: Cation (Ba, Ca, K, Mg, Na, Mn) concentrations were higher in the Spring River than the tributaries. Sulfate concentrations were generally low (≤ 60 mg/L) in the Spring River and even lower in the tributaries (Shoal Creek 2.0 - 20.0 mg/L). Concentrations of other water constituents were generally low throughout the river system. Three sites (Sites 1, 4, 5) in the Spring River had ammonia concentrations exceeding 0. mg/L. Nitrate levels were highest at Center Creek sites, ranging from 2.0 - 3.1 mg/L. Phosphorous concentrations were also generally low, with the highest concentrations found in the tributaries (Shoal Creek, 0.45- 0.76 mg/L; Center Creek, 0.22 - 0.47 mg/L).

Concentrations of metals in water and sediment indicated an overall enrichment in Center and Shoal Creeks, and in Empire Lake. Among the mining-derived metals of concern in the Spring River system, only zinc occurred at ICAP - detectable concentrations in surface waters (Tables 4 - 5). Zinc concentrations were generally higher in the tributaries (Shoal Creek, 17.4 94.9 $\mu g/L$; Center Creek, 171 -182 $\mu g/L$) than in the Spring River. The highest concentration (< 61.3 $\mu g/L$) occurred below the two tributaries and Empire Lake at Site 1 Concentrations of zinc in Shoal and Center creeks were similar to those reported in 1994 (49.4 - 153.0 $\mu g/L$ and 208 $\mu g/L$, respectively -- Schmitt et al. 1997).

The pattern for zinc in pore-water followed that of surface water; zinc concentrations in pore-water were greatest in Center Creek (197 - 1681 $\mu g/L$) (Table 6). Zinc concentrations were generally higher in Shoal Creek (36 - 87 $\mu g/L$) than in the Spring River except at Sites 1 and 5 which were below Center Creek (28 and 467 $\mu g/L$, respectively). Detectable concentrations of cadmium, lead, copper, and nickel were also found in pore-water at all sites (Table 6). Concentrations of cadmium and lead (2.6 $\mu g/L$ and 3.1 $\mu g/L$, respectively) were highest at the mouth of Center Creek -- Site 12. Cadmium concentrations increased from upstream (0.27 $\mu g/L$ at Site 11) to downstream (1.4 $\mu g/L$ at Site 2) in Shoal Creek. Copper concentrations were greatest in Shoal Creek (1.2 - 13.0 $\mu g/L$), at the mouth of Center Creek (2.0 $\mu g/L$), and at Spring River sites below Center Creek (1.6 - 1.8 $\mu g/L$) Concentrations of nickel were highest at Site 1 (15 $\mu g/L$) and at Site 8 in the mainstem of the Spring River (6.8 $\mu g/L$). Nickel concentrations were similar in Shoal Creek and Center Creek (3.6 - 5.7 $\mu g/L$ and 2.2 - 7.2 $\mu g/L$, respectively).

Iron concentrations were elevated at several sites in Center Creek (Sites 6 and 12 -- 1170 and 2240 mg/L, respectively), in the Spring River mainstem (Sites 1 and Site 8 -- 7760 and 14600 mg/L, respectively

Concentrations of mining-derived metals in sediments paralleled those found in surface and pore-waters (Tables 7 - 8). Lead and zinc concentrations were also higher in Center Creek (301- 2120 μg/g and 2060 - 13800 μg/g, respectively) and at those sites (Sites and 5) in the Spring River below Center Creek (69.5 - 138 μg/g and 659 - 1490 μg/g, respectively). Concentrations of lead and zinc were higher in Shoal creek (66.7 - 116 μg/g and 761 - 1160 μg/g, respectively) than at Spring River sites above Center Creek. Nickel concentrations were similar in the two tributaries and were generally higher than Spring River sites except those located downstream of Center and Shoal Creeks. Cadmium concentrations were below detection limits at sites in the Spring River except at Site 8, in the Spring River mainstem. The concentration of cadmium at Site 12 was much greater (84.1 μg/g) than any other site; aluminum and copper concentrations were also elevated at this site (160000 μg/g and 51.2 μg/g, respectively).

SEM and AVS analysis of the sediment was consistent with the ICAP analysis (Table 9-12). SEM / AVS ratios and SEM - AVS differences were calculated for elements which are known to form sulfides less soluble than the sulfide salts of iron or manganese, and are listed in Tables 10 - 11 Sediments having an SEM / AVS ratio > 1 and positive SEM - AVS differences are considered potentially toxic to organisms in the aquatic ecosystem

The SEM - AVS difference is generally more meaningful for samples with low AVS because it better reflects the magnitude of SEM metal excess (e.g., Site 3, Shoal Creek at the Sewage Treatment plant). Sediments having SEM / AVS rations less then should not be acutely toxic due to metals, but this does not preclude potential bioavailability of toxic metals through the food chain or if sediments become oxidized. No samples exhibited SEM / AVS ratios > 1 for cadmium or copper. Two samples from Shoal Creek (Sites 3 and 11) exhibited SEM / AVS ratios > 1 for nickel. Samples from these two sites, and Site 12 (Center Creek mouth) exhibited SEM / AVS ratios > 1 for lead, and all samples except the control site sediment (Tavern Creek) exhibited SEM / AVS ratios > 1 for zinc. In terms of SEM - AVS excess, two Center Creek sites (Site 12 and 6) had much greater values than two Shoal Creek sites (Sites 2 and 3) and the third site on Center Creek (Site 10). Metal excess at sites in the Spring River below the tributaries and the uppermost site in Shoal Creek were lower. Sites above the tributaries showed the smallest SEM - AVS excess.

Total Toxic Units were calculated for each site and are shown in Table 12. The site located at the mouth of Center Creek (Site 12) had the highest sum of Toxic Units (1427) as compared to the other sites (3.7 - 114). The Spring River site below Center Creek (Site 5, located near the mouth of Turkey Creek) had the second highest sum of Toxic Units. Zinc and nickel were bioavailable at all sites based on calculated Toxic Units. Lead was bioavailable at sites 3, 11, and 12, and cadmium was bioavailable at Site 12.

Distribution and Relative Dominance of Aquatic Macroinvertebrates: A total of 84 benthic macroinvertebrate taxa were identified from benthic samples collected during this study. Results are summarized in Table 13; the contents of individual samples are presented in Appendix A, Tables A5-A16. In general, the Spring River and its tributaries contain similar benthic compositions typical of late summer and autumn. The fauna of these systems can best be described by comparing individual tributaries, and considering sites on the Spring River above Center Creek (upper Spring River) separate from those sites located below Center Creek (lower Spring River). The upper Spring River and the uppermost site on Shoal Creek contained the highest number taxa representing the orders Ephemeroptera, Plecoptera, and Trichoptera--the so-called EPT taxa. The lower Spring River, Site 6 in Center Creek and Site 3 in Shoal Creek contained slightly lower numbers of EPT taxa. The lowest numbers of EPT taxa were observed in samples from the sites in Center Creek and the lowermost site in Shoal Creek. The reduced representation of EPT taxa in Center Creek, and the dominance of Chironomidae and nematodes in both tributaries suggests that water or habitat quality is degraded.

The benthic fauna of the Spring River was typically dominated by mayflies (Ephemeroptera) of the families Baetidae (*Baetis* sp.), Heptageniidae (*Stenonema* spp., *Stenacron interpunctatum*, *Leucrocuta* sp.), Tricorythidae (*Tricorythodes* sp.), Caenidae (*Caenis* sp.), and Potamanthidae (*Anthopotamus* sp.); net-spinning caddisflies (Trichoptera) of the family Hydropsychidae; predaceous stoneflies (Perlidae: *Neoperla* sp.); Chironmidae/Ogligochitae and riffle beetles of the family Elmidae (*Stenelmis* sp.). Additional taxa, such as water mites (Acarina), blackflies (*Simulium* sp.), micro-caddisflies (Hydroptilidae), Isopoda, Pelecypoda, and Nematoda, were occasionally dominant at some sites or in a few individual samples. Sites in the upper Spring River yielded the following taxa that were not collected at any other sites: *Ephron* sp. and *Leucrocuta* sp. (Ephemeroptera); *Perlinella ehyra* (Perlidae); *Sialis* sp. (Megaloptera); *Corbicula* sp. (Pelecypoda), and *Elima* sp. (Arachnoidea). *Antocha* sp. (Diptera) was the only taxon found exclusively in Center Creek, and *Atherix* sp. (Diptera) was the only species found exclusively in Shoal Creek.

Distribution and Relative Abundance of Fishes: A total of 29 fish species were found in the Spring River, Shoal Creek, and Center Creek. (Tables 14-16). Of these, sixteen were collected exclusively in the Spring River; the stippled darter (*Etheostoma punctulatum*) occurred exclusively in Center Creek Three species, the banded sculpin *(Cottus carolinae)*, longear sunfish *(Lepomis megalotis)*, and spotted bass (*Micropterus punctulatus*) were found only below Empire Lake at Site 1 The northern hogsucker (*Hypentelium nigricans*), speckled darter (*E. stigmaeum*), channel darter (*Percina copelandi*), western slim minnow (*Pimephales t tenellus*), channel catfish (*Ictalurus punctatus*), stonecat (*Noturus flavus*), and bluntface shiner (*Cyprinella camurus*) were only found at the upper Spring River sites. Densities of all species except cardinal shiner *(Luxilus cardinalis)* and slender madtom *(Noturus exilis)* were higher in the Spring River than in Center Creek or Shoal Creek.

The dominant fishes at all collection sites were minnows (Cyprinidae) of the genera *Notropis*, *Erimystax*, *Pimephales* and *Luxilus*; darters (Percidae); and native North American catfishes (Ictaluridae). Stonerollers (*Campostoma* spp.), cardinal shiners, rosyface shiners (*N. rubellus*) gravel chubs (*Erimystax X-punctatus*), northern orangethroat darters (*Etheostoma s. spectabile*), greenside darters (*E. blennioides*), and banded darters (*E. zonale*), occurred frequently in riffle samples from all sites. Other Percidae which were commonly found included the slenderhead darter *(Percina phoxocephala)*, fantail darter (*E. f flabellare*), and the ozark logperch (*P. c fulvitaenia*).

In the Spring River system, the slender madtom was the most common ictalurid. The stonecat (*N. flavus*), Neosho madtom, channel catfish (*I. punctatus*), and flathead catfish (*Pylodictis olivaris*) were found in only the Spring River.

Distribution and abundance of *N. placidus*: Neosho madtoms were found 4 of the 12 sites sampled Sites 1 ($n = 9$), 4 ($n = 6$), 5 ($n = 1$), and 9 ($n = 1$) (Tables 15 and 16). All of these sites were in the Spring River (Figure 1). Neosho madtoms were found at 9 of 19 mainstem sites in 1994 (Schmitt et al. 1997). No Neosho madtoms were collected at Site 5 (listed as Site 27) during in the 1994 study. Water in the eastern channel of the Spring River flowed north (upstream) around an island located at the mouth of Turkey Creek due to low flow in the Spring River, which resulted in this site being below the discharge from Turkey Creek in 1994. Both channels in the Spring River had flowing water in 1995, so Site 5 was not receiving water from Turkey Creek. The other six sites where madtoms had been collected in 1994 were not sampled in 1995 All of those sites were located above Center Creek.

Neosho madtoms considered to be young-of-the-year (y-o-y) were found at all sites except Site 9. Young-of-the-year madtoms had been collected at Site 9 in 1994 (listed as Site 23-Schmitt et al. 1997). Fish densities (0.38889 individuals / m^2) in the Spring River were similar to that found in 1994 (0.30 individuals / m^2).

Pore-water Toxicity Tests: Pore-water from two sites (Site 6, 12) in Center Creek and Site 1 were toxic to *C. dubia* (Table 17). All other sites had greater than 80% survival of adults. Toxicity results paralleled high concentrations of zinc in sediment, surface, and pore-waters at those sites and calculated Toxic Units.

Discussion

Concentrations of Mining-Derived Metals: The aquatic toxicity of lead, zinc, and cadmium are moderated by pH, alkalinity, and hardness. The chronic Water Quality Criterion for total recoverable zinc (C_{Zn}), lead (C_{Pb}) and cadmium (C_{Cd}), in μg/l, are defined in Appendix A, Table A1 with hardness in units of mg/L. Hardness in the Spring River and its tributaries was typically 130-175 mg/L (Table 3). As computed from the equation above, C_{Zn} = 149 µg/l at a hardness of 150 mg/L The Missouri Aquatic Life Criterion (MALC)--chronic for dissolved zinc in warm-water streams with a hardness of 125-200 mg/L is 340 μg/l (Missouri Department of Natural Resources 1992). Consequently, measured zinc levels in surface waters are potentially toxic to aquatic life at the four sites: All Center Creek sites (Sites 6, 10, 12) and the lowermost site in Shoal Creek (Site 2). Zinc concentrations in pore-waters exceed MALC at two Center Creek sites (Sites 6 and 12) and at the lowermost Spring River site (Site 1).

Concentrations of lead and cadmium in surface water were not detectable; however, dissolved lead concentrations of pore-waters averaged .6 μg/l, 1.33 μg/L, and 0.97 μg/L in the Spring River below Center Creek, in Center Creek and in Shoal Creek, respectively. Dissolved cadmium concentrations in pore-water averaged 1.8 μg/L, 0.88 μg/L, and 0.83 μg/L below Center Creek, in Center Creek and in Shoal Creek, respectively The chronic MALC for lead in warm-water streams of 125-200 mg/L hardness is 16 μg/L, and for dissolved cadmium it is 5 μg/l Generally, the chronic criteria incorporate bioaccumulation, and the dietary route of exposure is accounted for; nevertheless, the lead, zinc, and cadmium concentrations present at Spring River mainstem sites may be toxic, either individually or in combination, and especially if the benthic invertebrate food supply is heavily contaminated (e.g., Wildhaber et al. 1997, Woodward et al 1994).

Moss (1981) described the diet of larger adults as comprising invertebrates characteristic of mainstem riffles, mostly caddisflies (e.g., *Cheumatopsyche*, and *Hydropsyche*) and including mayflies (e.g., *Stenonema*, *Choroterpes*, and *Baetis*). Both young and adults feed extensively on dipterans. Although metal concentrations in benthic invertebrates were not examined, Wildhaber et al. (1997) found that concentrations of lead, zinc and cadmium in benthic invertebrates (e.g., Decapoda, Megaloptera) were highest at the mouth of Center Creek (Site 12), at the lowermost site in Shoal Creek (Site 2), at the mouth of Turkey Creek, and just downstream of Turkey Creek (Site 5). These concentrations, results of the toxicity tests and the Toxic Units analysis suggest that mining-derived metals in the lower reaches of the Spring River and its tributaries may be toxic to *N. placidus* and other aquatic organisms.

Present Distribution and Abundance of *N. placidus*: We found Neosho madtoms at Sites 1, 4, 5, and 9. Except for Site 1, these sites were all in the Missouri and Kansas portions of the Spring River mainstem, in the reach from the confluence of the mainstem and its North Fork, in Jasper County, Missouri downstream to the mouth of Turkey Creek, in Cherokee County, Kansas (Table 1, Fig. 1). Site 1 was situated in the West channel of the Spring River mainstem, downstream of Empire Lake and upstream of the confluence of Willow Creek, in Cherokee County. The collection of *N. placidus* at Baxter Springs and Waco confirmed collections made in 1994 (Wilkinson et al. 1996, Schmitt et al. 1997). As with other studies (Dames and Moore 1993b, Femmer and Joseph 1994), no Neosho madtoms were captured in either Spring River tributaries.

Fusilier and Edds (1994, 1995) reported the predominance of two length-age groups in the Cottonwood River population of Neosho madtoms during the period July-September: Young-of-the-year (y-o-y), which ranged in total length from 15 mm to about 40 mm; and age-which ranged from about 40 mm to 60 mm. Larger, age-3 fish also occurred, but rarely. In the Spring River, where we captured only 17 specimens, an accurate length-frequency distribution could not be developed; nevertheless, specimens characteristic of all three age-length classes were obtained (30 - 66 mm). Specimens of a size that could be considered y-o-y were collected at Sites 1, 4, and 5, where no apparent y-o-y had been collected in 1994 (Schmitt et al. 1997). No apparent y-o-y were collected at the Waco site (Site 9), although they were collected at this site in 1994 (Schmitt et al. 1997). The fish collected at Site 9 is considered at least an age-2 fish.

Toxic Units at Sites 1, 4, 9, where *N. placidus* were sampled, totaled less then units, and ranked ("1" having the lowest Total Toxic Units) 5, 3 and 1, respectively. Site 5 had the second highest sum of Toxic Units (114), which was an order of magnitude smaller then the highest sum (1427) found at Site 12. Toxicity tests, Toxic Units analysis, and chemical analysis suggest that Sites and 5 may be toxic to *N. placidus*. It is unknown whether these individuals are residents of this portion of the Spring River or whether they were washed downstream from upstream sites. Young-of-the-year ($n = 3$) were found below Empire Lake (Site 1) in 1995, which suggests that this population may be capable of reproduction and be self-sustaining. Only one individual was found at Site 5, which suggest that this population may be displaced from sites above Center Creek.

Fuselier and Edds (1994) found that Neosho madtoms generally do not leave riffle habitats which contain loosely embedded sediments. Organic material does not accumulate in this habitat as it does in depositional, backwater or pool habitats where our sediment and pore-water samples were taken. Toxic effects may be reduced due to less organic material, which enhances the mobility of bioavailable metals (Besser and Rabeni 1987). Concentration of metals may also be lower in riffle sediments, as seen in the pore-water collected from riffle habitats in 1994 (Wildhaber et al. 1996, Schmitt et al. 1997).

Summary and Conclusions

Collectively, studies conducted in the 1990's have confirmed the presence of a remnant, reproducing population of *N. placidus* in the Spring River in the reach from the confluence of the mainstem and North Fork, near Galesburg, Missouri downstream to Baxter Springs, Kansas (Wilkinson et al. 1996). The population persists in what may be the only remaining *N. placidus* habitat in the Spring River system. The most recent surveys have succeeded in finding Neosho madtoms on suitable gravel bars in the Waco-Baxter Springs reach when sampling has been conducted in late August and September. Sampling during other periods has been less successful (D. Edds, personal communication). Consequently, it is not possible to determine whether recent increases in the frequency of sightings in the Spring River reflect increasing numbers and expanding range, or simply that the whereabouts and habits of *N. placidus* are becoming better known and have been sampled more intensively in recent years. Toxicity tests, contaminant data, and analysis of the bioavailability of metals using the Toxic Units method suggest that the *N. placidus* population of the Spring River may be limited by mining-derived contaminants.

Acknowledgments: This study was jointly funded and undertaken by the U.S. Environmental Protection Agency, Region VII (EPA); the U.S. Department of the Interior (USDI), National Biological Service (NBS), now the Biological Resources Division of the U.S. Geological Survey, Environmental and Contaminants Research Center; and the USDI, Fish and Wildlife Service

(FWS), through its Ecological Services (ES) Field Office in Columbia, MO Assistance with field collections and data processing were provided by Phil Crockett, Phil Lovely, Brad Mueller, and Dave Whites of MSC; by Dave Munie contracted through EPA; Colette Charbonneau from FWS-ES Field Office in Columbia, Missouri; and Shane Ruessler from the NBS (formerly) Florida-Carribean Science Center, Gainesville, FL. Missouri Southern State College provided laboratory space throughout the study. In addition, we gratefully acknowledge the cooperation of the many private landowners in Kansas and Missouri who granted us permission to sample on their property

References

American Public Health Association (APHA) 1992. *Standard Methods for the Examination of Water and wastewater*. (18th Edition). Washington, DC, American Public Health Association.

Bednarik, A.F., and W.P. McCafferty. 1979. Biosystematic revision of the genus *Stenonema* (Ephemeroptera: Heptageniidae). Can. Bull. Fish. Aquat. Sci. No. 201. 73 pp.

Besser, J.M., and C.F. Rabeni. 1987. Bioavailability and toxicity of metals leached from lead-mine tailings to aquatic invertebrates. *Environ. Tox. and Chem.* 6:879-890.

Brown, H.P. 1972. Aquatic Dryopoid Beetles (Coleoptera) of the United States. Biota of Freshwater Ecosystems, Identification Manual #6 for U.S. EPA, Proj. No. 18050, Contract # 14-12-894. 82 pp.

Carr, R.S., and D.C. Chapman. 1995. Comparison of methods for conducting marine and estuarine sediment porewater toxicity tests- extraction, storage and handling techniques. *Arch. Environ. Contamin. Toxicol.* 28:(1):69-77.

Cross, F.B. 1967. Handbook of fishes of Kansas. Univ. Kansas Mus. Nat. Hist., Misc. Publ. No. 45. 45 pp.

Cross, F.B., and J.T. Collins. 1995. *Fishes in Kansas*. University of Kansas Natural History Museum, Public Education Series, No. 14. 315 pp

Czarneski, J. 1985 Accumulation of lead in fish from Missouri streams affected by lead mining. *Bull. Environ. Contam. Toxicol.* 34:736-745

Dames and Moore, Inc 1993a. Final remedial investigation for Cherokee County, Kansas CERCLA site, Baxter Springs/Treece subsites. Denver, Colo.

Dames and Moore, Inc 1993b. Draft site characterization memo: Neck/Alba, Snap, Oronogo/Duenweg, Joplin, Thoms, Carl Junction, and Waco Designated Areas, Jasper County Site, Jasper County, Missouri. Denver, Colo

Davis, J.V., and J.G. Schumacher 1992. Water quality characterization of the Spring River basin, southwestern Missouri and southeastern Kansas. U.S. Geological Survey, Water Resources Investigations Report 90-4176. Rolla, Mo. 112 pp.

DiToro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr, and M.S Redmond 1990. Toxicity of cadmium in sediments: the role of acid volatile sulfide. *Environ. Toxicol. Chem.* 9:1487-1502

Ferrington, L.C. Jr., O.K. Galle, M.A. Blackwood, C.A. Wright, W.A. Bird, J.M. Jobe, and P.B Grant. 1988. Preliminary assessment of cadmium, lead, manganese, and zinc in the Short Creek/Empire Lake aquatic system, Cherokee County, Kansas. Phase I. Kansas Water Resources Research Institute, University of Kansas, Lawrence. Contract No. 271 88 pp.

Fusilier, L., and D. Edds. 1994. Seasonal variation in habitat use by the Neosho madtom (Teleostei: Ictaluridae: *Noturus placidus*). *Southwest Natur.* 39(3): 217-223

Fuselier, L., and D. Edds. 1995. An artifical riffle as restored habitat for the Threatened Neosho madtom. *N. A. J. Fisheries Management.* 15:499-503

Hamilton, K., And E.P. Bergersen 1984. Methods to estimate aquatic habitat variables. U.S. Fish and Wildlife Service, Cooperative Fishery Research Unit, Colorado State University, Fort Collins, Colo. 70 pp.

Lee, D.S., C.R. Gilbert, C.H. Hocutt, R.E. Jenkins, D.E. McAllister, and J.R. Stauffer, Jr. 1980. *Atlas of North American freshwater fishes.* N.C. State Museum of Natural History, Raleigh. 866 pp.

Lewis, P.A. 1974. Taxonomy and Ecology of *Stenonema* mayflies (Ephemeroptera: Heptageniidae). U.S. Environmental Protection Agency, Cincinnati, Ohio. Environmental Monitoring Series Report EPA-670/4-74-006. 89 pp.

Mayden, R.L. 1988. Systematics of the *Notropis zonatus* species group, with description of a new species from the Interior Highlands of North America. *Copeia* 1988:153-173

Merritt, R.W., and K.W. Cummins. 1984. *An introduction to the aquatic insects of North America*. Kendall/Hunt, Dubuque, Iowa. 722 pp.

Morihara, D.K., and W.P. McCafferty. 1979. The *Baetis* larvae of North America (Ephemeroptera: Baetidae). *Trans. Amer. Entomol. Soc.* 105:139-221

Moss, R. 1981 Life history information for the Neosho madtom (*Noturus placidus*). Kansas Department of Wildlife and Parks, Contract No. 38. 28 pp.

Neuberger. J.S., M. Mulhall, M.C. Pomatto, J. Sheverbush, and R. Hassenein. 1990. Health problems in Galena, Kansas: A heavy metal mining Superfund site. *Sci. Total Environ.* 94:261-272.

Pennak, R.W. 1989. *Fresh-water Invertebrates of the United States: Protozoa to Mollusca.* John Wiley & Sons, Inc. New York. 803 pp.

Pflieger, W.L. 1975. *The fishes of Missouri*. Missouri Department of Conservation, Jefferson City.

Pita, F.W., and N.J. Hyne. 1975. The depositional environment of zinc, lead, and cadmium in reservoir sediments. *Water Res.* 9:701-706.

Plafkin, J.L., M.T. Barbour, K.D. Porter, S.K. Gross, and R.M. Hughes. 1989. Rapid bioassessment protocols for use in streams and rivers. U.S. Environmental Protection Agency, Washington, D.C. EPA/444/4-89-001

Platts, W.S., W.F. Megahan, and G.W. Minshall 1983. Methods for evaluating stream, riparian, and biotic conditions. Gen. Tech. Rep. INT-138. USDA Forest Service, Intermountain Forest and Range Experiment Station, Ogden, Utah. 70 pp.

Poulton, B.C., and K.W. Stewart 1991 The Stoneflies of the Ozark and Ouachita Mountains (Plecoptera). *Mem. Amer. Entomol.* Soc #38. 116 pp.

Proctor, P.D., G. Kisvarsanyi, E. Garrison, and A. Williams. 1974. Heavy metal content of surface and ground waters of the Springfield-Joplin area, Missouri. *In* D.D. Hemphill (ed.), *Proceedings of the 7th Annual Conference on Trace Substances in Environmental Health.* University of Missouri-Columbia, p. 63.

Robinson, H.W., and T.M. Buchanan. 1988. *Fishes of Arkansas.* University of Arkansas Press, Fayetteville. 536 pp.

Schefter, P.W., and G.B. Wiggins. 1986. A systematic study of the Nearctic larvae of the *Hydropsyche morosa* group (Trichoptera: Hydropsychidae). Life Sciences Misc. Pub., Royal Ontario Museum Issn 0082-5093

Schmitt, C.J., M.L. Wildhaber, A.L. Allert, and B.C. Poulton. 1997. The Effects of Historic Zinc-Lead Mining and Related Activities in the Tri-State Mining District on Aquatic Ecosystems Supporting the Neosho Madtom, *Noturus placidus*, Jasper County, Missouri; Ottawa County, Oklahoma; and Cherokee County, Kansas. Final Report to the U.S. Environmental Protection Agency, Region VII, Kansas City, Kansas. 88 pp.

Schmitt, C.J. 1994a. The effects of historic zinc-lead mining and related activities on ecosystems supporting the Neosho madtom, *Noturus placidus*, in Jasper County, MO; Ottawa County, OK; and Cherokee County, Kansas. National Biological Service, Midwest Science Center, Columbia, Mo. Study Plan No. 40095. 20 pp.

Schmitt, C.J. 1994b. Quality assurance project plan for the effects of historic zinc-lead mining and related activities on ecosystems supporting the Neosho madtom, *Noturus placidus*, in Jasper County, MO; Ottawa County, OK, and Cherokee County, KS. National Biological Service, Midwest Science Center, Columbia, Mo. 46 pp.

Schmitt, C.J., M.L. Wildhaber, J.B. Hunn, M.N. Tieger, B.L. Steadman, and T. Nash 1993a. Biomonitoring of lead-contaminated Missouri streams with an assay for δ-aminolevulinic acid dehydratase (ALA-D) activity in fish blood. U.S. Fish and Wildlife Service, National Fisheries Research Contaminant research Center, Columbia, Mo. Report to the U.S. Fish and Widlife Service, Region 3, Columbia, MO. 43 pp.

Schmitt, C.J., M.L. Wildhaber, J.B. Hunn, M.N. Tieger, B.L. Steadman, and T. Nash. 1993b. Biomonitoring of lead-contaminated Missouri streams with an assay for δ-aminolevulinic acid dehydratase (ALA-D) activity in fish blood. *Arch. Environ. Contam. Toxicol.* 25:464-475

Smith, B.J. 1988 Assessment of water quality in non-coal mining areas of Missouri. U.S Geological Survey, Water Resources Investigations Report 87-4286. Rolla, Mo. 50 pp.

Spruill, T.B. 1987. Assessment of water resources in lead-zinc mined areas in Cherokee County, Kansas, and adjacent areas. U.S. Geological Survey, Water-Supply Paper 2268. Lawrence, Kansas. 68 pp.

Thorp, J.H., and A.P. Covich. 1991. *Ecology and Classification of North American freshwater invertebrates.* Academic Press, San Diego, Calif. 911 pp.

U.S. Environmental Protection Agency. 1984a. Ambient water quality criteria for: Mercury. EPA 440/5-80-058. Washington, D.C

U.S. Environmental Protection Agency. 1984b. Ambient water quality criteria for: Lead. EPA 440/5-84-027. Washington, D.C.

U.S. Environmental Protection Agency. 1984c. Ambient water quality criteria for: Cadmium. EPA 440/5-84-032. Washington, D.C

U.S. Environmental Protection Agency. 1987. Ambient water quality criteria for: Zinc. EPA 440/5-87-003 Washington, D.C.

Wenke, T.L., and M.E. Eberle. 1991. Neosho madtom *Noturus placidus* Taylor recovery plan. Natural Science Research Associates, Hays, KS, for the U.S. Fish and Wildlife Service, Denver, Colo. 42 p.

Wiederholm, T. 1983. Chironomidae of the Holarctic region. Keys and Diagnosis. Part I--Larvae. *Entomol. Scand. Suppl.* 19:1-457.

Wildhaber, M.L., C.J. Schmitt, and A. L. Allert. 1997. Elemental Concentrations in Benthic Invertebrates collected from the Neosho, Cottonwood, and Spring Rivers. Final Report to the U. S. Fish and Wildlife, Region 6, Manhattan, Kansas. 17 pp.

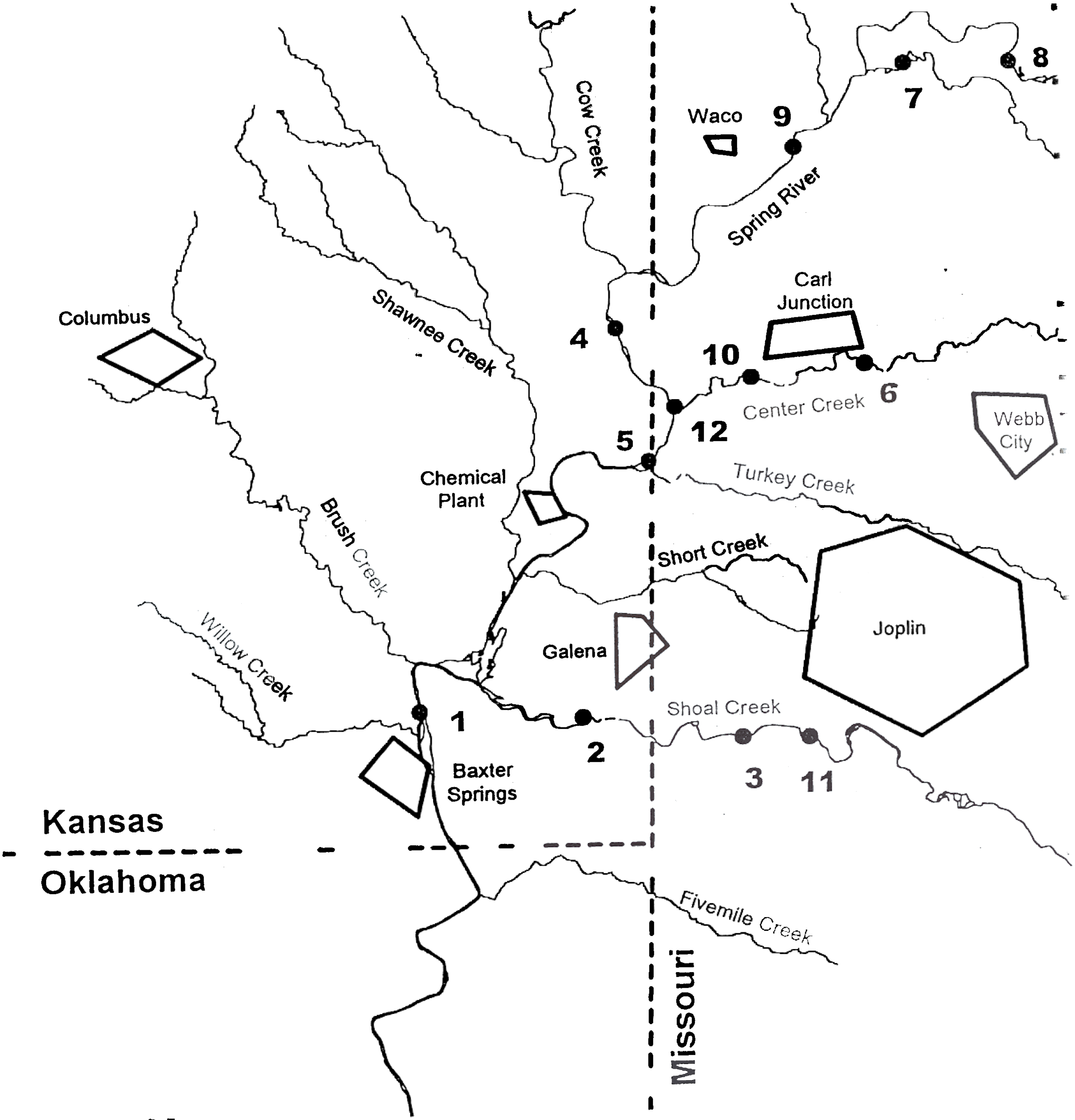
Wildhaber, M.L., C.J. Schmitt, and A.L. Allert. 1996. Historic Zinc-Lead Mining and Related Activities and their Effects on Aquatic Ecosystems Supporting the Neosho Madtom, *Noturus placidus*, Jasper County, Missouri; Ottawa County, Oklahoma; and Cherokee County, Kansas. Final Report to the U.S. Environmental Protection Agency, Region VII, Kansas City, Kansas. Appendix A: Tables A1- A35. 221 pp. Appended July, 1997.

Wildhaber, M.L., and C.J. Schmitt 1996. Estimating aquatic toxicity as determined through laboratory tests of Great Lakes sediments containing complex mixtures of environmental contaminants. *Environ. Monit. Assess.* 41:255 - 289.

Wilkinson, C., D. Edds, J. Dorlac, M.L. Wildhaber, C.J. Schmitt, and A. Allert. 1996. Neosho madtom distribution and abundance in the Spring River. *Southwest Natur.* 41(1):78-81

Williams, J.E., J.E. Johnson, D.A. Hendrickson, S. Contreras-Balderas, J.D. Williams, M. Navarro-Mendoza, D.E. McAllister, and J.E. Deacon. 1989. Fishes of North America endangered, threatened, or of special concern, 1989. *Fisheries* 14:2-20.

Woodward, D.F., W.G. Brumbaugh, A.J. DeLonay, E.E. Little, and C.E. Smith. 1994. Effects on rainbow trout fry of a metals-contaminated diet of benthic invertebrates from the Clark Fork River, Montana. *Trans. Am. Fish. Soc.* 123:51-62.



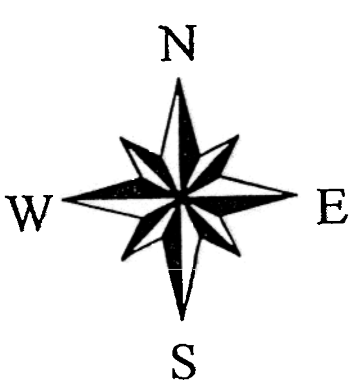


Figure 1. Map of the Spring River system illustrating Collection sites. See Table 1 for site descriptions.